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Crystallization of silver chromate from ethanol via salt metathesis reactions of solubilized precursors

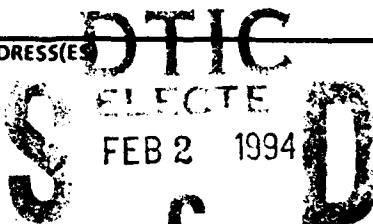
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## 13. ABSTRACT (Maximum 200 words)

Admixture of aqueous solutions of silver nitrate and potassium chromate results in immediate precipitation of silver chromate as a red-brown microcrystalline powder, while addition of aqueous silver nitrate solution to a solution of potassium chromate/18-crown-6 in ethanol gives a bright-red precipitate. X-ray powder diffraction shows both materials to be orthorhombic silver chromate. The ethanol-derived sample displays broader diffraction peaks, suggesting smaller crystallite size. Scanning electron microscopy confirms this. The ethanol-derived sample appears amorphous, while the aqueous sample displays well-faceted crystallites approximately 0.5 - 1 micron in size.

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Crystallization of silver chromate from ethanol via salt metathesis reactions of solubilized precursors

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Interim Technical Report

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## **Experimental**

Two samples of silver chromate ( $\text{Ag}_2\text{CrO}_4$ ) were prepared by admixture of solutions of  $\text{AgNO}_3$  and  $\text{K}_2\text{CrO}_4$ :

Sample A:  $\text{AgNO}_3$  solution in water added dropwise to solution of  $\text{K}_2\text{CrO}_4$  in water, resulting in immediate precipitation of a red-brown powder. This was isolated by filtration and washed with water, then ethanol, then diethyl ether, affording the  $\text{Ag}_2\text{CrO}_4$  as a brown powder in high yield.

Sample B:  $\text{AgNO}_3$  dissolved in 0.5 mL water, then diluted with 4 mL ethanol and added dropwise to a solution of  $\text{K}_2\text{CrO}_4$  in ethanol (6 mL) containing 3 equivalents of 18-crown-6, resulting in immediate precipitation of a red powder. This was isolated by filtration and washed with ethanol, then water, then ethanol, then diethyl ether, affording the  $\text{Ag}_2\text{CrO}_4$  as a red powder in high yield.. (Note that  $\text{K}_2\text{CrO}_4$  appears completely insoluble in ethanol in the absence of 18-crown-6.)

Each sample was examined by x-ray powder diffraction and shown to be the (known) orthorhombic phase of  $\text{Ag}_2\text{CrO}_4$ . Each appeared crystalline; however, sample A (prepared from water) appeared to be composed of significantly larger crystallites, as evidenced by sharper lines in the powder diffraction pattern.

Scanning electron microscopy confirmed this observation: Sample A was comprised entirely of apparently well-faceted crystallites approximately 0.5 - 1 micron in size, while sample B displayed no clearly identifiable crystallites, being composed instead of aggregates of visually amorphous (but, recall, still crystalline as shown by x-ray powder diffraction) material.

## **Discussion**

Silver chromate serves an important role as a cathode material for nonaqueous-electrolyte batteries. It has also appeared in the patent literature as an alkene polymerization catalyst, as a potential optical recording material, and as a component in anti-fouling agents. It is generally prepared by a simple metathesis reaction between, e.g., potassium chromate and silver nitrate. Such metathesis reactions are universally carried out in aqueous solution, as the precursors display negligible solubility in nonaqueous solvents. We have found that use of 18-crown-6 as a complexing agent allows preparation of solutions of potassium chromate in ethanol. Dropwise addition of ethanolic silver nitrate (containing a few percent water in order to solubilize the silver salt) to such an ethanolic solution of solubilized potassium chromate results in immediate precipitation of silver chromate which, as demonstrated by visual inspection (color of the bulk sample), X-ray powder diffraction, and electron microscopy, is of significantly smaller crystallite size than silver chromate prepared from aqueous solution. The ability to effect such a significant alteration in crystallite size simply through alteration of crystallization medium, made possible through application of our technique of complexation-mediated crystallization, may prove of profound importance in, e.g., the area of semiconductor nanoparticle technology.